PATENT SPECIFICATION 744,074

Date of Application and filing Complete Specification: June 8, 1953.

No. 15770/53.

Application made in United States of America on June 12, 1952.

Complete Specification Published: Feb. 1, 1956.

Index at Acceptance:—Class 1(3) A1D(10:30), A1G34D1O, A1G37D(10:30).

COMPLETE SPECIFICATION

Improvements in or relating to the purification of titanium tetrachloride

We, NATIONAL LEAD COMPANY, a Corporation organised and existing under the Laws of the State of New Jersey, United States of America, of 111, Broadway, New York 6, State of New York, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention is for improvements in or relating to the purification of titanium tetrachloride.

In general the tetrahalides of metals of the fourth group of elements are prepared by chlorinating a metal bearing material and recovering the metal tetrachloride vapour in the form of a relatively impure liquid condensate. By way of example, liquid titanium tetrachloride is commonly prepared by treating a titaniferous material such as titaniferous iron ore, or ilmenite with chlorine gas, in a static bed or fluo-solids operation, to form titanium tetrachloride vapour which is subsequently condensed to form a crude titanium tetrachloride condensate. Since there are a number of elements in the raw material, in addition to titanium, which react with chlorine to form volatile chlorides and which carry over with the titanium tetrachloride vapours, the titanium tetrachloride condensate, sometimes hereinafter referred to as crude titanium tetrachloride, is invariably impure. Moreover, it has been found that these volatile chlorides are not readily eliminated by distillation since the respective chlorides such as, for example, the chlorides of silicon, aluminium, niobium, tungsten and vanadium, tend to distil over with the titanium tetrachloride values and to be found in the condensate. One such impurity which, because of the proximity of its boiling point to that of titanium tetrachloride, cannot be separated therefrom by fractional distilation is vanadium chloride. Vanadium chloride is present in substantially all crude titanium tetrachloride condensate and comprises a major portion of the impurities in the condensate and hence is chiefly responsible for the yellowish colour of crude titanium tetrachloride. By way of example, a typical crude titanium tetrachloride may comprise from 0·25 to 0·35% vanadium based on the weight of the titanium tetrachloride the other impurities being present in relatively small amounts such as, for example, from 0·04 to 0·2% silica, from 0·02 to 0·025% alumina, from 0·01 to 0·02% niobium and from 0·05 to 0·08% tungsten.

While it has been proposed heretofore to purify crude titanium tetrachloride and other similar tetrahalides by treatment with such materials as hydrogen sulphide, silica gel, carbon, salts of the heavy metals, soya bean oil and art gum, such methods have been characterized by the formation of residues which have been either insoluble or removable from the still bottoms only with the greatest difficulty. As a consequence the adaptation to commercial production of prior methods for purifying crude titanium tetrachloride have been attended by much difficulty and high cost.

An object of the invention is, therefore, to provide a superior method for purifying crude titanium tetrachloride which is convenient, economical and adapted to commercial production.

A still further object of the invention is to provide a superior method for removing a major portion of the impurities from crude titanium tetrachloride in a manner such that no polymerization occurs and the residue formed may be readily removed from the still.

[*Price 3s. 0d.*]

According to the present invention there is provided a process for purifying crude titanium tetrachloride to remove a major portion of the impurities therefrom which comprises refluxing the crude titanium tetrachloride in the presence of animal waxes in the proportion of not more than 0·2% based on the weight of the crude titanium tetrachloride.

As used herein the term animal wax sometimes hereinafter referred to as a purifying agent, has reference to a specific group of waxes indentified in the Table of Constants of Fats, Oils and Waxes on page 678 of Lang's Handbook of Chemistry, 5th Edition, published by the Handbook Publishers, Inc., namely:

Wool fat (wax).
Spermaceti.
Beeswax.

The animal waxes have been found to serve as a highly satisfactory purifying agent for crude titanium tetrachloride; and to form a non-polymerized residue.

The treatment of crude titanium tetrachloride, by which is meant a liquid titanium tetrachloride containing impurities such for example as vanadium, silica, alumina, niobium and tungsten, with the animal wax may be carried out, in any convenient manner which will ensure the required intimacy of contact between the crude titanium tetrachloride and the purifying agent. Preferably the purification treatment is carried out in a purification unit comprising, for example, a still having a fractionating column, a reflux return and a condenser, by heating the crude titanium tetrachloride with an animal wax in the still to a temperature and for a period of time such that substantially all of the titanium tetrachloride is circulating as vapour through the fractionating column and reflux return, and thereafter allowing the vapour to pass to the condenser in which the titanium tetrachloride will be condensed and collected as a water-white liquid. The heating of the liquids and recirculation of the vapour is sometimes hereinafter referred to as refluxing.

The residue which forms in the bottom of the still is generally a relatively hard granular substance which may be readily removed from the still and which, before being washed, has been identified by X-ray patterns as comprising a mixture of rutile, anatase, free carbon and impurities the principle one of which is vanadium.

The aforesaid relatively hard granular residue comprises titanium dioxide, vanadium, and small amounts of silica, alumina, tungsten, niobium and other impurities the vanadium being in the form of VCl_3 and/or $VOCl_3$ which may be recovered from the residue by water leaching. It has been observed that the vanadium content of crude liquid titanium tetrachloride may be reduced by the process of this invention from about 0·35% by weight of titanium tetrachloride as found in crude titanium tetrachloride to about 0·0001%, the purified liquid titanium tetrachloride being water-white.

The term "water-white" is used herein to denote a substantially pure titanium tetrachloride condensate. In particular a titanium tetrachloride condensate purified by the process of this invention and defined as water-white is one having a major portion of its impurities removed i.e. the maximum vanadium content is in the range of from about 0·0001% to 0·0003% by weight of the titanium tetrachloride, the remaining impurities in the titanium tetrachloride condensate being present in such small quantities as to be innocuous.

The time and temperature of treatment is dependent to some extent upon the amount of impurities in the crude titanium tetrachloride and upon the amount of the purifying agent used to remove the impurities from the titanium tetrachloride. Moreover, the amount of the purifying agent used is, in turn, dependent upon the amount of impurities and in particular the amount of vanadium present in the crude titanium tetrachloride.

In carrying out the treatment of the crude titanium tetrachloride, the animal wax is usually added to crude titanium tetrachloride at substantially room temperature whereupon the mixture is heated to a temperature of from 134°C to 138°C for a period of time, generally in the neighbourhood of about 2 hours, after which the titanium tetrachloride vapours are condensed to form substantially water-white titanium tetrachloride. The length of time necessary for effective treatment of the crude liquid titanium tetrachloride varies inversely with the amount of animal wax added to the crude titanium tetrachloride. For economical reasons a minimum amount of animal wax for effecting substantially complete purification of the crude titanium tetrachloride is preferred and where a minimum amount of animal wax is added such as, for example, substantially 0·1% based on the weight of the crude titanium tetrachloride the time required for refluxing the mixture of crude titanium tetrachloride and the animal wax is about 2 hours. However, it has been observed that when the amount of animal waxes is substantially 0·2% then the reflux time is about 1 hour. In short as the amount of purifying compound added to the crude titanium tetrachloride is increased the time required for refluxing the admixture of crude titanium tetrachloride and the purifying compound is decreased.

Following is a description by way of example of methods of carrying the invention into effect.

EXAMPLE

0·1 part of wool fat was added to 100 parts of crude titanium tetrachloride at substantially room temperature, refluxed at a temperature of about 136°C for a period of 2 hours, and distilled to yield a clear water-white titanium tetrachloride.

By the process of this invention crude titanium tetrachloride comprising impurities the major portion of which is vanadium may be purified by refluxing the titanium tetrachloride in the presence of an animal wax wherein a relatively small quantity of the animal wax is required and a substantially pure water-white titanium tetrachloride condensate is produced in an economical, convenient and commercially practical manner.

What we claim is:

1. A process for purifying crude titanium tetrachloride to remove a major portion of the impurities therefrom which comprises refluxing the crude titianium tetrachloride in the presence of animal waxes in the proportion of no more than 0·2% based on the weight of the crude titanium tetrachloride.

2. A process as claimed in claim 1 wherein the impurities comprise vanadium, a mixture is formed of the crude titanium tetrachloride and the animal waxes and the mixture is refluxed at a temperature and for a period of time sufficient to produce a water-white titanium tetrachloride condensate.

3. A process as claimed in either of the preceding claims wherein the animal wax is spermaceti.

4. A process as claimed in claim 1 or claim 2 wherein the animal wax is beeswax.

5. A process as claimed in claim 1 or claim 2 wherein the animal wax is wool fat.

6. A process as claimed in any one of the preceding claims wherein the proportion of animal waxes is substantially 0·1% based on the weight of crude titanium tetrachloride.

7. A process as claimed in any one of the preceding claims wherein the mixture is refluxed at a temperature of approximately 136°C. for a period of approximately 2 hours.

8. A process for purifying crude titanium tetrachloride substantially as described with reference to the specific example hereinbefore set forth.

BOULT, WADE & TENNANT,
111 & 112, Hatton Garden, London, E.C.1,
Chartered Patent Agents.

Printed by Her Majesty's Stationery Office Press, 55–57, Drury Lane, W.C.2.—1956
Published at the Patent Office, 25, Southampton Buildings, London, W.C.2, from which copies may be obtained